Distribution of excited atoms in non-equilibrium plasma of noble gases

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A system of nonlinear equations is solved by a numerical method. Phase diagrams that are the diagrams of meta-equilibrium states for Ar, Xe, Kr are presented. Characteristic distributions of excited states of the stationary argon plasma and experimental distributions of excited states of yttrium obtained from the spectra of erosive plasma jet of a high-current discharge in a capillary tube are presented.

Introduction

The LTE (local thermodynamic equilibrium) approximation is usually used in spectroscopic diagnostics of low-temperature plasma and in the study of plasma of active laser media.$^{1-3}$ In this case the distribution of atoms over excited states (DES) is described, in the logarithmic scale, by a straight line. The slope of this strait line determines the so-called temperature of DES that coincides with the electron temperature.

In tackling the problems, which assume electron collisions take the dominating part in the processes of energy exchange, other processes being neglected, the distributions of particles over energy states obey the LTE model and Maxwell, Boltzmann, and Saha formulas do apply.^{2} The majority of problems in plasma diagnostics are being solved within the LTE model.

In non-equilibrium plasma or, in accordance with Ref. 4, not LTE plasma the DES deviates from the Boltzmann distribution. In several cases, see, for example, Refs. 5–7, the DES has a form of a broken curve. The population of energy states is described, accurate to the errors, by two straight lines having different slopes.

According to Ref. 8, the probability distribution of a complex system reduces to a product of factors, each factor describing only one part of the system. So, these parts are already considered to be statistically independent. This statement is correct^8 if f_1 and f_2 are two physical values relating to two different subsystems so that the average value of the product $f_1 f_2$ equals to the square root from the product of average values of f_1 and f_2 taken separately:

$$\overline{f_1 f_2} = \sqrt{\bar{f}_1 \bar{f}_2}. \tag{1}$$

This means that if the Boltzmann distribution establishes in an infinitely long time then at shorter time intervals other distributions can exist, thus representing the entire distribution by a broken line within the segments of which the equality (1) for the average values holds.

Distribution of excited atoms in the collisional-radiation model

Let us turn to one of the first publications^9 having a direct relation to creation of plasma lasers. As in all theoretical models of plasma lasers, that followed this one, the time-dependent kinetics equations are self-consistent owing to the heat balance equations for the temperature of electrons. Special value is placed on the conversion of ion into a molecular ion followed by the dissociation recombination. In considering such problems theoretically the gas temperature T_g (it is not equal to the electron temperature T_e), the collision frequency (pump frequency) ν, and the pressure are the initial parameters. Under quasi-stationary approximation for the supercooled helium plasma the important dependences of the temperature and concentration of electrons N_e and atomic ions of helium N^+ on the concentration of helium N (or on the number of nuclei N_n) have been obtained, see Fig. 1.

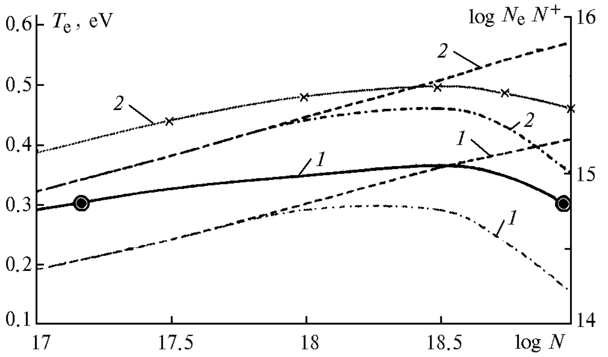

Fig. 1. Dependence of the temperature and concentration of electrons and atomic ions of helium on its concentration N. Solid line shows the dependence T_e, the dashed one shows the dependence on N of concentration of atomic ions. The curves correspond to the following pump parameters^9 (s^{-1}): curve *1* to ν = 100; *2* to ν = 1000.

Note that identical electron temperatures are characteristic of the same pump frequency, but different pressures, i.e., various N, which differ by a factor of one and a half or two orders of magnitude.

Similar dependences can be obtained in a different statement of the problem, when the gas temperature T_g, concentration of electrons N_e (but not the pressure), and the electron temperature, $T_e \approx$ const, are the initial parameters of the problem.[10,11]

In some publications[10,11] the stationary system of nonlinear kinetics equations for isolated levels has been solved by a numerical method for a single-component gas allowing for the radiation transitions, excitation by an electron collision, and conversion of ions into the molecular ions followed by the dissociation recombination. The relaxation (64 × 64) matrix is constructed for 64 levels and thereby takes into account ~ 3000 reactions.

The peculiarity of notations used in Ref. 10 in the system consists in that it enables to exclude the concentrations N^+ and N_2^+ and to obtain the equation for the population vector only. As a result, the solution is a diagram of meta-equilibrium states (see Fig. 2) that establish one-to-one correspondence between the concentration of electrons N_e and the number density of nuclei N_n (N_0) at a given temperature of electrons T_e. In Figure 2 the point *1* corresponds to the LTE model, point *2* to the collisional-radiation meta-equilibrium state (CRmS).[7] The second approach makes it possible to construct DES for 64 levels and investigate them.

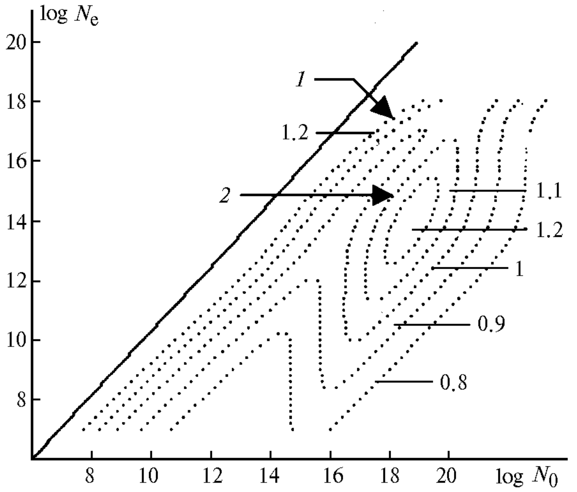

Fig. 2. The diagram of meta-equilibrium states of argon plasma (T_e, eV).

Let us restrict our consideration of the interaction processes between the atoms and electrons to such processes as the inelastic collisions of the 1st and 2nd kind (2), ionization (3), and a threefold recombination (4), where N_i is the population of the ith state (i = 1, 2, 3, ..., 64):

$$N_i + e \leftrightarrow N_j + e, \tag{2}$$

$$N_i + e \rightarrow N^+ + 2e, \tag{3}$$

$$N^+ + 2e \rightarrow N_j + e. \tag{4}$$

In this case DES does not differ topologically from the Boltzmann distribution (Fig. 3) both at large and small N_e values, however, the numerically the populations differ by orders of magnitude at $\log N_e < 16$.[7] The curve *4* in Fig. 3 is obtained for values denoted by figure 1 in Fig. 2, where the LTE model is assumed to be valid.

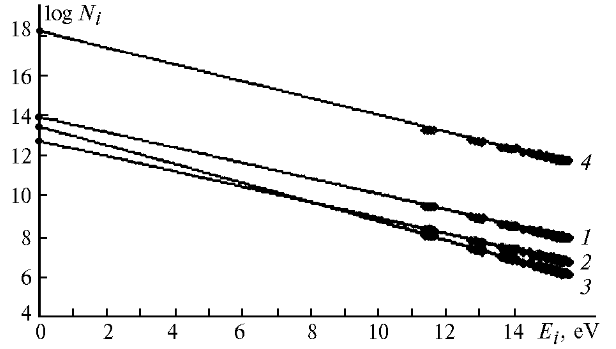

Fig. 3. DES allowing for the electron processes by the formulas (2)–(4): (*1*) T_e = 1.1 eV, $N_e = 10^{15}$ cm^{-3}, $N_0 = 10^{15.02}$ cm^{-3}; (*2*) T_e = 1.1 eV, $N_e = 10^{14.4}$ cm^{-3}, $N_0 = 10^{14.41}$ cm^{-3}; (*3*) T_e = 0.9 eV, $N_e = 10^{14}$ cm^{-3}, $N_0 = 10^{14.06}$ cm^{-3}; (*4*) T_e = 1.1 eV, $N_e = 10^{17}$ cm^{-3}, $N_0 = 10^{18.2}$ cm^{-3}.

If reactions of conversion and the following dissociation recombination are included into the consideration

$$N^+ + 2N_1 \rightarrow N_2^+ + N_{1j} + e, \tag{5}$$

$$N_2^+ + e \rightarrow N_i + N_1, \tag{6}$$

then a solution also appears at the point *2* in the diagram (see Fig. 2). In this case the topology of DES changes in principle (as it will be shown in Fig. 5). The DES (for argon), which are solutions of the stationary system of the kinetics equations for isolated levels and refer to the case of collisional-radiation meta-equilibrium can be characterized by three parameters, which are analogous to temperature of electrons under LTE conditions. The populations of excited states of the low levels depending on their excitation energies are located at the same straight line (in the logarithmic scale) and have the excitation temperature $T_{\text{exc}}^{(1)}$; the populations of the next group of the dependences on the excitation energy are located on the straight line with the excitation temperature $T_{\text{exc}}^{(2)}$. The excitation temperature of the levels neighboring the continuum $T_{\text{exc}}^{(3)}$ equals to the temperature of electrons T_e. The following condition is fulfilled

$$T_e = T_{\text{exc}}^{(3)} > T_{\text{exc}}^{(1)} > T_{\text{exc}}^{(2)}.$$

The authors of Refs. 5 and 6 have chosen an identical scheme of the energy levels in argon (n = 64), take equally into account the electron and photon processes but in contrast to Ref. 10 they do not include into consideration the reactions (5) and (6). In the calculations made in Ref. 6 the escape of particles to the wall and the loss of meta-stable states due to conversion into the excited molecules are taken into account, for which reason the system of equations becomes nonlinear. The nonlinearity of the kinetic equations[6,10] is caused by different reactions and, in spite of this, the DES topology has same character.

It should be emphasized that the condition (1) is satisfied: the square root of the product of temperatures corresponding to the “brokenB DES $\sqrt{T_{\text{exc}}^{(1)}\,T_{\text{exc}}^{(2)}}$ equals to the temperature of the Saha-Boltzmann distribution.

DES and the ARC discharge in argon

In the known publication by V.N. Kolesnikov[12] the arc discharge in argon at atmospheric pressure with the small admixture of hydrogen has been investigated. Figure 4 presents its temperature relations (solid curves) obtained by different methods: the solid curve *1* was obtained from the relative measurements of the electron temperature T_e using bremsstrahlung radiation; the solid curve *2* corresponds to the excitation temperature according to populations of the argon levels relative to the ground state; the curve *3* is obtained from Saha formula; the solid curve *4* is the temperature of excitation that follows from the populations of high levels.

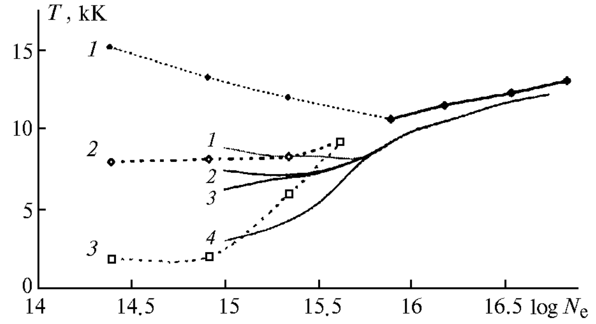

Fig. 4. The temperatures measured in the argon plasma (arc discharge for 1 atm).

In the monograph 13 only two curves from Fig. 4 are presented: the curves *1* and *4*, and the curve *1* is interpreted as a change of electron temperature depending on the concentration of electrons N_e (it is impossible to do not agree with this), and *4* is attributed to the gas temperature (this is not obvious).

The calculations of the levels’ kinetics in argon allowing for the reactions (2)–(6) confirm the behavior of the experimental temperature dependences (see Fig. 4, dashed lines). The DES, by which the temperature dependences were calculated, are presented in Fig. 5*b*, *c*, and *d*. The DES curves *1* correspond to the parameters indicated nearby.

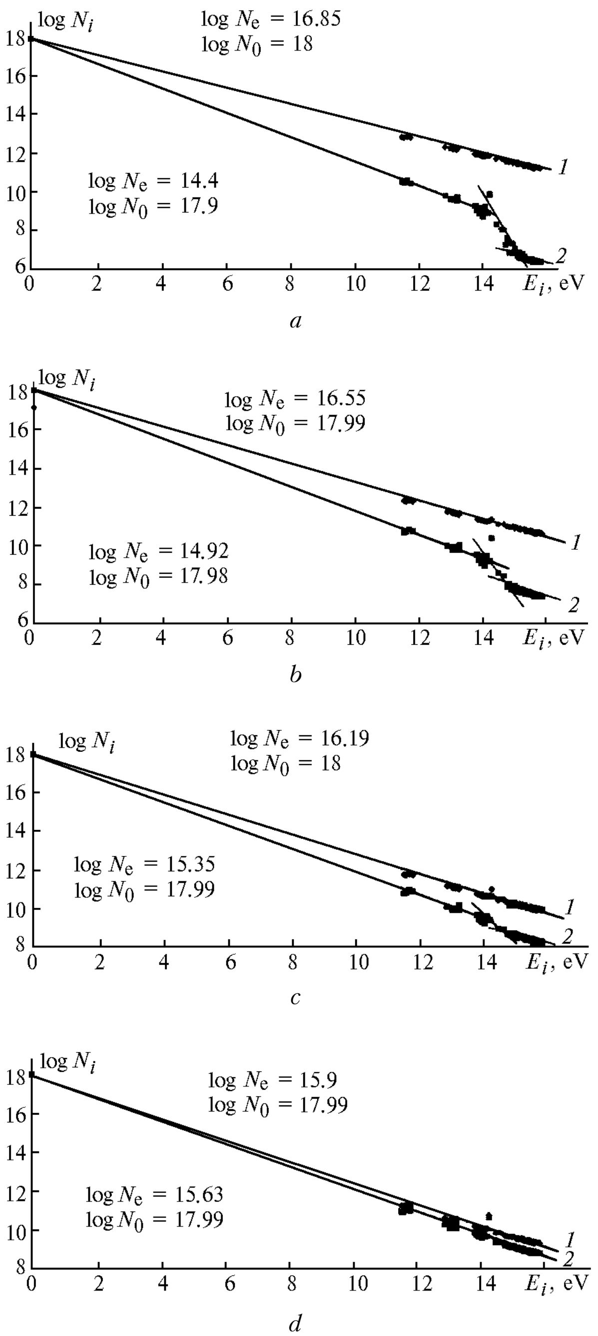

Fig. 5. DES in argon: *a*: $T_e = 1.1$ eV, (*1*) $N_e = 10^{16.85}$ cm^{-3}, $N_0 = 10^{18}$ cm^{-3}, (*2*) $N_e = 10^{14.4}$ cm^{-3}, $N_0 = 10^{17.9}$ cm^{-3}; *b*: $T_e = 1.05$ eV, (*1*) $N_e = 10^{16.55}$ cm^{-3}, $N_0 = 10^{17.99}$ cm^{-3}, (*2*) $N_e = 10^{14.92}$ cm^{-3}, $N_0 = 10^{17.98}$ cm^{-3}; *c*: $T_e = 2.0$ eV, (*1*) $N_e = 10^{16.19}$ cm^{-3}, $N_0 = 10^{18}$ cm^{-3}, (*2*) $N_e = 10^{15.35}$ cm^{-3}, $N_0 = 10^{17.99}$ cm^{-3}; *d*: $T_e = 0.97$ eV, (*1*) $N_e = 10^{15.9}$ cm^{-3}, $N_0 = 10^{17.99}$ cm^{-3}, (*2*) $N_e = 10^{15.63}$ cm^{-3}, $N_0 = 10^{17.99}$ cm^{-3}.

“StratificationB of the temperatures that may be seen in Fig. 4 shows that instead of a unified distribution, corresponding to the temperature curve *3*, there appeared two quasi-subsystems with their own DES and temperature curves *2* and *4*. For these subsystems the condition (1) is satisfied.

Conclusion

The solution of system of the nonlinear equations of the levels' kinetics of plasma in noble gases has been carried out by a numerical method. The main result of the investigation is the diagrams of meta-equilibrium states obtained from analysis of stationary nonlinear differential equations. Instead of Saha formula we have the diagram of meta-equilibrium states that establishes the one-to-one correspondence among the density, electron concentration, and electron temperature.

In the quasi-stationary regime the quasi-equilibrium is possible. Populations of the excited states of low levels as functions of their excitation energy are located at the same straight line (in the logarithmic scale) and have the excitation temperature $T_{\rm exc}^{(1)}$; the populations of the next group of levels as functions of their excitation energy are on the straight line with the temperature $T_{\rm exc}^{(2)}$; the excitation temperature of the levels neighboring the continuum $T_{\rm exc}^{(3)}$ equals to the temperature of electrons $T_{\rm e}$. The condition $T_{\rm exc}^{(3)} > T_{\rm exc}^{(1)} > T_{\rm exc}^{(2)}$ is fulfilled. The calculated values of $T_{\rm exc}^{(1)}$ and $T_{\rm exc}^{(2)}$ are confirmed experimentally under conditions of a stationary arc discharge.

The theoretical model discussed well suits analysis of the non-equilibrium plasma in quasi-stationary problems. Non-linearity of the system of equations causes the "brokenB behavior of DES which, as we suppose, can be considered not only from the standpoint of a single set of atomic excited states but from the standpoint that admits existence of two independent quasi-subsystems.

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